

1 **TITLE**

2 High Contrast Surface Marking Using Irradiation of  
3 Electrostatically Applied Marking Materials  
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7 **CROSS REFERENCES TO RELATED PATENTS**  
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9 This application is a continuation-in-part of U.S. App.  
10 Ser. No. 09/477,921, filed January 5, 2000 and now issued as  
11 U.S. Pat. No. \_\_\_\_\_, which is a divisional application of  
12 U.S. App. Ser. No. 08/925,031, filed September 8, 1997 and  
13 issued as U.S. Pat. No. 6,075,223 on June 13, 2000.  
14 International application PCT/US98/18720, filed on September  
15 8, 1998 and published as WO 99/16625 on April 8, 1999,  
16 claimed priority from USSN 08/925,031.  
17

18 **FIELD OF INVENTION**

19 The present invention relates to a method of producing  
20 permanent, enhanced contrast and/or color markings formed as  
21 a new marking layer on top of substrates including glass,  
22 ceramic, porcelain, metal, and plastic. A laser beam or  
23 other suitable radiant energy source irradiates a marking  
24 medium having a glass frit containing an energy absorbing  
25 enhancer, or alternatively the marking medium can be a mixed  
26 metal oxide or a mixed organic pigment. This invention  
27 further relates to a method of producing permanent enhanced  
28 contrast and/or color markings formed as a new marking layer  
29 on top of both electrically conductive and non-conductive  
30 substrate materials by electrostatically coating said  
31 substrate materials and irradiating said coating with a  
32 laser beam in accordance with the form of a mark or  
33 decoration to be produced. In particular, this invention

1 pertains to the application of laser marking materials in a  
2 controlled pattern of finely separated, charged coating  
3 particles projected toward an electrically-isolated and/or  
4 oppositely-charged substrate material.

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#### BACKGROUND OF THE INVENTION

7 The marking of ceramic materials, glazes and glasses  
8 can be effected by conventional marking and decoration  
9 methods such as etching, cutting, engraving, grinding or by  
10 applying a glass or glaze colorant. In these methods, the  
11 surface of the marked material is altered with the  
12 consequence that the material may suffer damage, especially  
13 if marking is effected by etching, engraving, or cutting.  
14 The application of a glass or glaze colorant necessitates,  
15 in addition, a second firing step. The markings so produced  
16 are not always satisfactory in all respects.

17 It is also known to mark glass by means of a laser  
18 beam, whereas the known methods are based on melting or  
19 removing substrate material such that the surface of the  
20 marked material is also altered.

21 German Offenlegungsschrift 3 539 047 postulates a  
22 method of decorating, marking, and engraving enameled  
23 objects using laser beams by incorporating into the enamel  
24 coating opacifying agents which the laser beam causes to  
25 decompose optically and locally; for example, oxides of  
26 titanium, tin, cerium, and antimony. A drawback of this  
27 method is that, for example, transparent enameled objects  
28 cannot be marked because the opacifying agent incorporated  
29 in the enamel coating does not change optically at the non-  
30 irradiated areas and, therefore, strongly influences the  
31 overall appearance of the object. Furthermore, the  
32 opacifying agent employed may adversely affect the  
33 mechanical properties of the enamel.

1 Industry has sought to surface mark glass, ceramic,  
2 porcelain, metal, plastics, and the like with four physical  
3 attributes. These four attributes are high-resolution,  
4 high-contrast, permanence, and speed.

5 Well known efforts to date have only produced two or  
6 three of these attributes. For example, kiln marking  
7 ceramics using glass frit material at kiln temperatures  
8 ranging from 100° to 1000° C results in high-resolution,  
9 high-contrast, permanent indicia on ceramics, glass, and  
10 metals. These known processes require heating the entire  
11 substrate along with the glass frit or metal oxide marking  
12 material in a kiln. The problem with these processes is the  
13 time factor and energy consumption are not commercially  
14 efficient to create the indicia. Time factors ranging from  
15 minutes to hours are common. Energy consumption of a kiln  
16 is generally measured in kilowatts per ton and/or BTUs per  
17 pound. Furthermore, these processes do not lend themselves  
18 to portability.

19 Another known marking method is peening on metal. This  
20 method cannot be used on glass, ceramic, or other brittle  
21 materials because of surface damage and/or breakage. Where  
22 used, this method produces a high-resolution, permanent,  
23 fast surface indicia. However, high contrast marks are not  
24 produced.

25 Other known marking methods are ink printing methods.  
26 One state of the art transfer printing method is taught by  
27 WO 95/13195 (May 1995) to Meneghini et al, assigned to  
28 Markem Corporation. These methods use a laser-transferable  
29 ink on a plastic carrier. The ink is mixed in a transfer  
30 medium solution in order to enhance the conversion of laser  
31 (IR) energy to heat. These methods produce a high-  
32 resolution, high-contrast, and relatively fast method.  
33 There is a UV cure step which is time consuming. The

1 problem with this and all ink methods is a lack of  
2 permanence. Acids and other solvents remove ink from a hard  
3 surface. This method teaches curing the ink onto the  
4 substrate surface. *The present invention teaches bonding a*  
5 *marking medium to form a new marking layer atop the*  
6 *substrate surface rather than transferring an ink to the*  
7 *substrate and then curing the ink.*

8 Another well known marking method teaches the use of  
9 ink jet printers. In order to improve application  
10 performance, appearance and permanence, environmentally  
11 hazardous solvents are mixed with the ink. Even with these  
12 hazardous solvents however, significant improvement has not  
13 been achieved.

14 U.S. Pat. No. 4,541,340 (1985) to Peart et al.  
15 discloses a printing process for marking fabrics or plastics  
16 in a permanent image. Sublimable dyes are used such as  
17 nitroso dyes. A diffusion of the dyestuff into the  
18 substrate is caused by a pressurized air step on a transfer  
19 label. Only application to fabrics and plastics is taught.  
20 The chemistry is different from the present invention.  
21 However, the result of a permanent high contrast mark is  
22 claimed.

23 Another related group of marking methods is laser  
24 combined with glass frit or metal oxide marking media. U.S.  
25 Pat. No. 4,769,310 (1988) to Gugger et al. teaches first  
26 creating a glaze in a kiln process. The glaze has a  
27 radiation sensitive additive in amounts ranging from .01 to  
28 30% by weight. This glaze is then irradiated by a beam of  
29 Nd:YAG pulsed laser having light pulses of six to eight  
30 nanoseconds at a wavelength of 0.532  $\mu\text{m}$  and a pulse content  
31 of 250 milli-joules. The problem with this method is the  
32 burden of creating a time consuming glaze surface before  
33 applying the high-speed laser beam.

1 U.S. Pat. No. 5,030,551 (1991) to Herren et al. teaches  
2 a laser-based method to mark ceramic materials, glazes,  
3 glass ceramics, and glasses by first applying to a workpiece  
4 a 100 to 10,000 Angstrom thick transparent layer of titanium  
5 dioxide. Second, the workpiece is fired in an oven at 620°  
6 C for one minute and then slowly cooled in the closed oven.  
7 Third, the layer is irradiated with a pulsed laser in  
8 accordance with the form of the marking to be applied. The  
9 laser light must have a wavelength which is sufficiently  
10 absorbed by the oxide layer so that a discoloration of the  
11 oxide layer is produced at the irradiated areas. The  
12 problem with this method is the time and energy-consuming  
13 step of firing and cooling the workpiece.

14 The method of the present invention makes it possible  
15 to produce a direct and rapid marking that is indelible and  
16 which is, therefore, abrasion and scratch-proof. The  
17 markings obtained are also corrosion-proof, solvent-  
18 resistant, dimensionally stable, free from deformation, fast  
19 to light, heat, and weathering, easily legible, and have  
20 good contrast and very good edge definition. In addition,  
21 there is virtually no impairment of the mechanical,  
22 physical, and chemical properties of the marked material,  
23 e.g. mechanical strength and chemical resistance.

24 There has now been found a flexible method which makes  
25 it possible to mark metals, plastics, ceramic materials,  
26 glazes, glass ceramics and glasses without damaging the  
27 surface thereof and without specific requirements being made  
28 of the substrate, which method comprises the use of a glass  
29 frit based or mixed organic materials or mixed metal oxide  
30 layer for the laser marking.

31 Accordingly, the present invention relates to a method  
32 of radiantly marking both conductive and dielectric  
33 materials including metals, plastics, ceramic materials,

1 glazes, glass ceramics and glasses of any desired form which  
2 comprises steps of applying to the substrate material a  
3 marking material which, depending upon its principal  
4 components, may or may not contain at least one energy  
5 absorbing enhancer, then irradiating said marking material  
6 layer with a laser or diode based energy source such that  
7 the radiation is directed onto said layer in accordance with  
8 the form of the marking to be applied, and using laser or  
9 diode based energy of a wavelength which is sufficiently  
10 absorbed by the marking material so that a bonding occurs on  
11 the substrate, thereby forming a marking layer atop the  
12 substrate.

13 A preferred embodiment of the present invention employs  
14 electrostatic methods of applying marking materials to the  
15 substrates. The principles behind electrostatics have been  
16 applied in the development of electrophoresis, powder  
17 coating sprayers, xerography and ink jet printers.  
18 Electrostatic coating technology has been available for many  
19 years and is widely used for the coating of household  
20 appliances such as ranges, refrigerators, washing machines  
21 and dryers. There are some subtle aspects to this science  
22 such as fine atomizing of liquid droplets, fine de-  
23 agglomerating and diffusion of powders, eliminating or  
24 shielding unintended target areas, creation of an optimal  
25 electrical charge on the part surface as well as optimizing  
26 part geometry and orientation. Characteristics of  
27 electrostatic coating processes include low energy  
28 expenditure, absence of pollution or other undesirable  
29 effluents, and high material utilization efficiencies. Its  
30 applications reduce waste and improve manufacturing  
31 efficiency and product quality. There are no apparent  
32 adverse secondary effects from application of  
33 electrostatics.

1 Behind the operation of all electrostatic coating  
 2 equipment is the fundamental principle that oppositely  
 3 charged bodies attract one another. Therefore, charged  
 4 marking material particles would be attracted towards a  
 5 grounded or oppositely-charged article. In the  
 6 electrostatic coating process, the target substrate is  
 7 grounded so that it is electrically neutral. The coating  
 8 system creates, electrically charges, and disperses solid  
 9 particles or liquid droplets of the marking material toward  
 10 the target substrate by a variety of methods well known to  
 11 one skilled in the art. The charged marking material  
 12 particles are attracted to the grounded, neutral substrate  
 13 and are deposited on it. Since the charged particles are  
 14 all charged alike they repel from each other during the  
 15 flight to the target and while "landing". These marking  
 16 material particles avoid each other and seek areas on the  
 17 target surface that are best grounded (i.e. uncoated areas).  
 18 This is one of the simplest and most elegant aspects of the  
 19 electrostatic coating process: deposition is uniform because  
 20 the least coated areas get coated by the "newest" particles.  
 21 The use of electrostatic deposition technology means that  
 22 very good reproducibility and precision of deposition can be  
 23 obtained - relative standard deviations (RSDs) of 1-2  
 24 percent of coating thickness can be achieved. This is a  
 25 significant improvement and tremendous advantage over  
 26 conventional coating methods.

27 Since the article being coated is the collecting  
 28 electrode in the electrostatic coating process, it should  
 29 have sufficient electrical conductivity, either through its  
 30 bulk or across its surface, to carry away the electrical  
 31 charge arriving on the surface with the accumulating marking  
 32 material particles. For this reason, the electrostatic

1 coating process is most often used to coat objects which are  
2 natural conductors of electricity (e.g. metals).

3 Typically, such conductive articles are held at a  
4 grounded potential by merely being supported from a grounded  
5 conveyor with a metal hook. By induction from the charging  
6 electrode, the conductive article assumes an electrical  
7 charge, which is opposite to that of the charged marking  
8 material particles. Accordingly, the electrically  
9 conductive article attracts the charged marking material  
10 particles.

11 Notwithstanding the above, electrostatic coating  
12 practices are also used to coat articles made from non-  
13 conductive or dielectric materials (e.g. plastics, glass,  
14 ceramics, wood, etc.), hereinafter collectively referred to  
15 as "dielectric materials". When used for these purposes, it  
16 becomes necessary to make the dielectric material either a  
17 permanent or temporary electrical conductor. A number of  
18 techniques have been perfected to accomplish this objective  
19 and these methods are well known to one skilled in the art.

20 For example, molded rubber steering wheels are not  
21 natural conductors of electricity; however, they can be made  
22 electrically conductive by heating them to temperatures of  
23 at least about 212° F. (100° C.). While this practice works  
24 well for electrostatically coating some dielectric  
25 materials, it has a number of problems associated therewith.  
26 For example, this practice cannot be used to induce a charge  
27 on those dielectric materials which do not become  
28 electrically conductive when heated (e.g., wood). Moreover,  
29 this practice also cannot be used to induce a charge on  
30 those dielectric materials, which begin to deform or degrade  
31 at or below the temperature needed to make them electrically  
32 conductive.



1 Another method of electrostatically spraying a  
2 dielectric material consists of coating the material with an  
3 electrically conductive primer. This practice is used in  
4 the coating of toilet seats. Specifically, toilet seats are  
5 normally made from a phenolic resin/wood-flour mixture.  
6 This material is non-conductive and does not become  
7 conductive upon heating. Accordingly, to make it possible  
8 to electrostatically coat these items, the seats are first  
9 sprayed with an electrically conductive, film forming  
10 primer. When dried, this coating creates an electrically  
11 conductive film on the surface of the seat. After being  
12 coated with this primer, the seats are supported from a  
13 grounded conveyor with metal hooks. Thereafter, the marking  
14 materials could be electrostatically applied.

15 Electrostatic coating methods are disclosed in many  
16 patents.

17 U.S. Pat. No. 2,622,833 discloses a process and  
18 apparatus for electrostatically coating the exterior  
19 surfaces of hollow articles made from a dielectric or non-  
20 conductive material without the use of backing electrodes,  
21 which conform to the shape of the article. In that patent,  
22 the articles being coated are mounted onto spindles, which  
23 are connected to a conveyor system. The conveyor and the  
24 spindles are electrically conductive. Moreover, they are  
25 both connected through a conductor to either a ground or a  
26 power supply.

27 In U.S. Pat. No. 2,622,833, a conductive probe, which  
28 has an ionizing point or points, is electrically connected  
29 to the spindles. This probe is positioned so that it  
30 passes, through the article's opening, into the cavity of  
31 the article being coated. The spindles then carry these  
32 articles between oppositely disposed, spaced negatively-  
33 charged electrodes. As the articles pass the electrodes, an

1 electrostatic field is created between the negatively-  
2 charged electrodes and the exterior surface of the article.  
3 One or more spray guns are directed so as to introduce an  
4 atomized coating composition in a direction generally  
5 parallel to the path of travel of the articles into the  
6 space between the articles and the electrodes. As the  
7 marking material particles enter into the ionizing zone,  
8 they accept a negative charge and are thus drawn to the  
9 grounded or positively-charged article.

10 U.S. Pat. No. 4,099,486 also discloses a process and  
11 apparatus for electrostatically coating glass bottles by  
12 using a particular chuck for supporting the bottles which is  
13 designed to prevent build-up of coatings thereon. That  
14 patent induces a charge onto the glass bottles by heating  
15 them to a temperature ranging between 150° F. (66° C.) to  
16 450° F (232° C.). According to U.S. Pat. No. 4,099,486, the  
17 supporting chuck is made from a non-conductive plastic.  
18 This chuck fits over a grounding plug, which is designed to  
19 ground the bottle by being in physical contact therewith.  
20 For example, one embodiment of a ground plug described in  
21 that patent is in the form of a flat-headed probe upon which  
22 rests the neck of the bottle. Another embodiment of a  
23 ground plug described in that patent is in the form of a  
24 flat-ended rod which extends into the bottle's opening, and  
25 through the bottle's entire length, until the distal end of  
26 the rod contacts the inside surface of the bottle's base.  
27 Yet another embodiment of a ground plug described in that  
28 patent is in the form of a flat-ended rod whose outside  
29 dimension is parallel to the inside dimension of the  
30 bottle's opening. With this latter configuration, when the  
31 ground plug is inserted into the bottle's opening, the  
32 outside walls of the plug contact the inside walls of the

1 bottle's neck. Additional patents disclosing electrostatic  
2 coating methods and apparatus include:

3 U.S. Pat. No. 6,063,194 (Dry Powder Deposition  
4 Apparatus)

5 U.S. Pat. No. 5,830,274 (Electrostatic Deposition of  
6 Charged Coating Particles onto a Dielectric Substrate)

7 U.S. Pat. No. 5,698,269 (Electrostatic Deposition of  
8 Charged Coating Particles onto a Dielectric Substrate)

9 U.S. Pat. No. 4,099,486 (Electrostatically Coating  
10 Hollow Glass Articles)

11 U.S. Pat. No. 4,110,486 (Electrostatic Powder Coating  
12 Method)

13 U.S. Pat. No. 3,930,062 (Composition and Method for  
14 Electrostatic Deposition of Dry Porcelain Enamel Frit)

15 U.S. Pat. No. 3,558,052 (Method and Apparatus for  
16 Spraying Electrostatic Dry Powder).

17 Fully integrated electrostatic coating systems are  
18 commercially available for efficient coating of small parts  
19 in laboratory and batch-production operations from companies  
20 such as Trutec Industries, Powder Spray Technologies, Double  
21 D Equipment Company and Wagner International. To coat small  
22 parts, use of an electrostatic or hot-dip fluidized bed  
23 system can provide efficient coating quality. An  
24 electrostatic fluidized bed can be used for either  
25 electrostatic deposition or for hot-dip coating of small  
26 parts, and can operate with just a few ounces of marking  
27 materials.

#### 28 29 **SUMMARY OF THE INVENTION**

30 The main aspect of the present invention is to provide  
31 a method to quickly, with high-resolution, high-contrast,  
32 and permanence, mark the surface of a workpiece.

1 Another aspect of the present invention is to provide a  
2 method to irradiate a marking material which may or may not  
3 contain at least one energy absorbing enhancer, wherein the  
4 marking material is selected from the group consisting of  
5 glass frits, glass frits with ceramic colorants, and glass  
6 frits with porcelain enamels, where the workpiece is a  
7 conductive or dielectric material such as glass, ceramic,  
8 porcelain, certain metals, and certain plastics. (Clear  
9 glass and glass frits do not absorb energy in the 1 micron  
10 range of the Nd:YAG or diode lasers, but do absorb energy in  
11 the 10 micron range, so these materials may not require  
12 additional energy absorbing enhancers.)

13 Another aspect of the present invention is to provide a  
14 method to irradiate a marking material containing metal  
15 compounds including mixed metal oxides where the workpiece  
16 is metal, glass, ceramic, porcelain and certain plastics.

17 Another aspect of the present invention is to provide a  
18 method to irradiate a marking material containing mixed  
19 organic pigments where the workpiece is plastic, glass,  
20 ceramic, porcelain and certain metals.

21 Another main aspect of the invention related to all of  
22 the above aspects is to provide various electrostatic  
23 methods of applying the marking materials to the substrate  
24 to be marked.

25 Other aspects of this invention will appear from the  
26 following description and appended claims, reference being  
27 made to the accompanying drawing forming a part of this  
28 specification wherein like referenced characters designate  
29 corresponding parts in the drawing.

30 Thus, in accordance with the present invention, a  
31 series of thermally activated, chemically based marking  
32 methods are provided, comprising steps of:

1       electrostatically applying a layer of an energy  
2 absorbing marking material to a conductive or dielectric  
3 substrate to be marked; and

4       irradiating the layer of marking material with a  
5 radiant energy beam having a wavelength selected to excite  
6 the energy absorbing material in accordance with the form of  
7 a marking to be applied, thereby forming a marking layer  
8 atop the substrate. The objective is generally to provide a  
9 bonded and permanent marking atop the substrate which is  
10 visible in contrast with the substrate.

11       When electrostatically applying the marking material to  
12 dielectric substrates, a conductive layer of material is  
13 normally first applied to the substrate.

14       The irradiation process can be improved by providing a  
15 laminar air flow across the substrate during the irradiating  
16 step which maintains a consistent environment by carrying  
17 away any gasses created during the irradiating step of the  
18 inventive process, and preferably is started at an ambient  
19 temperature of about 70 deg. F.

20       The marking material can comprise a variety of  
21 substances which can be tailored to the substrate, but must  
22 contain at least one component which will absorb sufficient  
23 radiant energy to cause the marking material to fuse or  
24 sinter and create a permanently bonded marking upon the  
25 substrate. In some cases an energy absorbing enhancer such  
26 as carbon black can be included in the marking material.  
27 The marking materials can include various metal compounds  
28 including oxides, mixed oxides, sulfides, sulfates,  
29 carbonates, carbides, nitrides and silicides. Colorants can  
30 be included, as described below. The marking material can  
31 also include various types of glass frit material, alone or  
32 in combination with various metal compounds.

1       The substrates can comprise a variety of conductive and  
2 dielectric materials selected from suitable metals, glasses,  
3 ceramics and plastics.

4       Prior to the present invention, no quick and permanent  
5 method existed for marking certain substrate materials with  
6 enhanced contrast and/or color which would also permit the  
7 rapid change of content and/or information in the mark  
8 without structural damage to the substrate material. In  
9 theory, an optical power source, properly focused, could  
10 create the same temperatures obtained by ovens and/or kilns  
11 used in conventional "firing" processes involving marking  
12 materials. The speed of computer controls for the optical  
13 power source, the beam steering mechanism and the mark  
14 content make it possible for individual enhanced contrast  
15 and/or color marks to be bonded to the various substrate  
16 materials in extremely short time periods without structural  
17 damage in a way not attainable by any other marking or  
18 decorating process. The wide variety of marking materials  
19 make it possible to produce images with varying optical  
20 properties including, but not limited to, contrast, color,  
21 reflectance, diffraction; and varying physical properties  
22 including, but not limited to, thickness, durability,  
23 stability, structural shape and electrical conductivity.

24       The present inventive process of permanently marking  
25 materials will be especially useful in marking glass,  
26 ceramic, porcelain, and other brittle materials whose  
27 surface structure cannot withstand the thermal shock of  
28 other commonly used high-power pulsed laser marking methods.  
29 In the present invention, the resulting images on all  
30 substrate materials have enhanced contrast and/or color  
31 which makes the mark more easily viewed and imaged by the  
32 human eye and/or machine vision equipment and is highly  
33 resistant to chemical and mechanical wear. This feature is

1 a great advance in barcode and 2D symbology marking, since  
2 the prior art high-power pulsed laser-only marking systems  
3 cannot always create sufficient contrast and/or color  
4 markings.

5 This invention relates to the permanent bonding of  
6 enhanced contrast and/or colored materials to the surfaces  
7 of various conductive or dielectric materials including  
8 glass, ceramic, porcelain, metal, and plastic substrates  
9 using radiant energy produced by, but not limited to,  
10 optical power sources such as lasers, laser diodes, direct  
11 diodes and diode-pumped lasers. The sun's radiant energy,  
12 properly filtered and focused, could make an acceptable  
13 radiant energy source. The wavelength ( $\lambda$ ) and output power  
14 (watts) of the optical power source are determined by the  
15 combination of the composition of the substrate material and  
16 the natural or enhanced energy absorbing characteristics of  
17 specific marking material to be applied. The marking  
18 materials are formulated to react with various substrate  
19 materials at certain temperatures. The radiant energy  
20 source can produce the required temperatures in small  
21 localized areas within microseconds and create an  
22 environment where the desired chemical and mechanical  
23 reactions will occur. Virtually any computer-generated mark  
24 can be produced on a substrate by moving the beam emanating  
25 from the radiant energy source on the marking material on  
26 the surface of the workpiece using conventional beam  
27 steering mechanisms and/or X - Y plotter mechanisms and/or  
28 by moving the workpiece relative to a stationary beam.

29 The marking material is electrostatically applied to  
30 the surface of the workpiece. The beam emanating from the  
31 radiant energy source impinges upon the marking material,  
32 which absorbs the radiant energy and elevates it to the  
33 required temperature. In absorbing the radiant energy, at

1 least a portion of the marking material is excited, i.e. has  
2 its atoms or molecules raised to an excited state. [See  
3 Webster's Encyclopedic Unabridged Dictionary of the English  
4 Language (Portland House, New York, 1989), page 497.]  
5 Typically , a temperature of 200° to 1500° F is reached in  
6 approximately one to two microseconds. Precise temperatures  
7 are controlled by the output power of the radiant energy  
8 source and the physical position of the marking material  
9 relative to the focal plane of the radiant energy beam and  
10 the speed with which the beam is moving. Once the required  
11 temperature is achieved, the marking material and substrate  
12 will permanently bond together to form a new marking layer  
13 atop the substrate. The interaction of the radiant energy  
14 and the marking material is believed to result in an inert  
15 coating mechanically and chemically bonded to the substrate  
16 material. The marking layer is believed to form covalent  
17 bonds with the substrate material, and it is believed this  
18 chemical bond exceeds the strength of the mechanical bond.  
19 Marking materials can be formulated to absorb specific  
20 amounts of a specified wavelength of the radiant energy.

21 CO<sub>2</sub> lasers are capable of permanently marking glass  
22 materials by thermally shocking the surface and causing  
23 fractured facets. These fractures are detrimental to the  
24 structural integrity of the glass and will continue to  
25 propagate, causing chips to fall out of the mark.  
26 Furthermore, the imaged mark has no enhanced contrast and is  
27 difficult to view or image. Certain organic materials  
28 (wood, plastic, etc.) are easily marked using CO<sub>2</sub> lasers,  
29 but the resulting imaged mark can only have limited color  
30 and/or contrast based on the material composition and the  
31 effect of the laser energy (it will cause burning of the  
32 surface). There are a number of specially formulated



1 plastic materials that will change color when exposed to  
2 specific laser energy and produce an enhanced contrast mark.

3 Nd:YAG lasers are generally capable of permanently  
4 marking a variety of metals and some organic materials.  
5 However, the same limited variation of color and contrast  
6 applies. Some steels and other hard metals can be burned  
7 with sufficient laser power to produce a dark mark against  
8 the natural surface color. However, the heat created by  
9 this method causes the area surrounding the mark to darken  
10 resulting in significantly decreased contrast.  
11 Additionally, very few color variations are possible. Most  
12 direct diodes cannot produce sufficient beam quality or  
13 power to achieve the same effects as the Nd:YAG lasers.

14 The principal advantages of the inventive process are:

- 15 - no structural damage to the substrate material  
16 surface;
- 17 - no post processing required to stabilize the  
18 finished mark;
- 19 - wide variety of colors, contrasts and physical  
20 properties;
- 21 - high resolution for the imaged mark;
- 22 - resistant to chemical and mechanical wear;
- 23 - marking speeds in seconds, not minutes or hours;
- 24 - image content can be changed at computer speeds;
- 25 - individual marks can be fully automated; and
- 26 - permanent markings will withstand flexing,  
27 expansion and contraction of substrate.

28 Features of the inventive process believed to be  
29 significant improvements are:

- 30 1) The use of laser or diode based radiation to  
31 rapidly elevate the temperature of the marking  
32 material atop the substrate to form a new marking  
33 layer atop the substrate.

- 1           2)    a single laser beam pass is all that is required.
- 2           3)    Selecting marking materials specially formulated
- 3                to react with specific substrate materials using
- 4                laser or diode based radiation as the catalyst.
- 5           4)    Speed with which the mark can be produced.
- 6           5)    Speed with which the content of the mark can be
- 7                changed.
- 8           6)    Method of delivery of marking material to the
- 9                substrate surface including various types of
- 10           electrostatic deposition.
- 11           7)    Marks can be applied to glass and other brittle
- 12                surfaces without fracturing.
- 13           8)    Enhanced contrast and/or color of mark.
- 14           9)    Two-, three-, or four-color images can be marked
- 15                with near photo quality.
- 16           10)   Elimination of any firing step of entire
- 17                workpiece.
- 18           11)   Ability to first ablate (if desired) and then mark
- 19                selected substrates to create 3D high-contrast
- 20                markings with a simple two-step process.
- 21           12)   Using relatively low-cost, low-contaminating
- 22                marking materials (glass frits, mixed metal
- 23                oxides, or mixed organic pigments) instead of
- 24                silver oxides or other high-cost highly-toxic
- 25                materials.
- 26           13)   Higher resolution of imaged mark (>1000 dpi).

27

28           A significant feature added by the present invention is

29   the use of various suitable electrostatic methods of

30   applying the marking materials to the substrates be

31   radiantly marked using radiant energy. As described above

32   in general and below in detail as to the present invention,

33   many electrostatic application methods are known to those in

1 the art, and suitable disclosures are found in many U.S.  
2 patents. In most cases where marking materials are to be  
3 applied to conductive materials such as metals, the marking  
4 materials can be directly applied in liquid, aerosol or  
5 finely-divided solid form to the substrate or other surface  
6 to be marked by suitable electrostatic methods. When  
7 dielectric materials such as glasses, ceramics, plastics and  
8 the like are to be marked, a conductive coating or layer  
9 should normally be applied to the surface before the marking  
10 materials themselves are electrostatically applied, as is  
11 well known in the art.

12 A more complete appreciation of the present invention,  
13 and many of the attendant aspects and advantages thereof,  
14 will be readily ascertained as the invention becomes better  
15 understood by reference to the following Detailed  
16 Description when considered with the accompanying Figures  
17 briefly described below.

#### 18 **BRIEF DESCRIPTION OF FIGURES AND EXAMPLES**

19 The following figures are incorporated by reference from  
20 the parent application, U.S. Serial No. 08/925,031, filed  
21 September 8, 1997 and issued as U.S. Pat. No. 6,075,223 on  
22 June 13, 2000, with FIG. 1 of that application omitted.

23 In all the below listed figures, the resulting marks  
24 were produced on commercially available Nd:YAG laser markers  
25 as manufactured, for example, by GSILumonics Corporation, A  
26 B Lasers, Inc., Control Laser, Inc., and/or Rofin Sinar,  
27 Inc. with power capability and optical configurations  
28 capable of providing the referenced marker parameters. In  
29 all examples the laser marker utilized produced a spot size  
30 of 100 to 125 microns, and the surface of the workpiece was  
31 placed 2mm to 3mm below the focal plane of the laser beam.  
32 In FIG. 1 through FIG. 7 the marking material was applied  
33

1 with resulting thicknesses between 75 and 125 microns on the  
2 workpiece surface.

3 FIG. 1 is a photograph of a stainless steel workpiece  
4 having the uppermost mark produced using Cerdec 29-1777  
5 Amber Stain mixed metal oxide mixed at a 1/1 ratio by weight  
6 with mineral oil as the marking material with the inventive  
7 process and exhibiting high contrast from all viewing angles  
8 with no detectable damage to the workpiece surface. The mark  
9 was produced using 5 watts of CW energy at a beam speed of  
10 200mm/second. The lower mark was produced using the same  
11 laser settings without the inventive process resulting in  
12 only an ablative laser process and a mark of varying  
13 contrast that is totally dependent upon the viewing angle.

14 FIG. 2 is a photograph of a polished stainless steel  
15 workpiece having the mark produced using Cerdec 29-1777  
16 mixed metal oxide mixed at a 1/1 ratio by weight with  
17 mineral oil as the marking material with the inventive  
18 process and exhibiting high contrast from all viewing angles  
19 with no detectable damage to the workpiece surface. The mark  
20 was produced using 5 watts of CW energy at a beam speed of  
21 200mm/second.

22 FIG. 3 is a photograph of an aluminum workpiece having  
23 the mark produced using 10 parts Cerdec 29-1060 mixed metal  
24 oxide combined with 1 part Cerdec 29-1777 mixed metal oxide  
25 and then mixed at a 1/1 ratio by weight with mineral oil as  
26 the marking material with the inventive process and  
27 exhibiting high contrast from all viewing angles with no  
28 detectable damage to the workpiece surface. The mark was  
29 produced using 5 watts of CW energy at a beam speed of  
30 200mm/second.

31 FIG. 4 is a photograph of an alumina ceramic workpiece  
32 having the mark produced using Cerdec 24-2702 glass frit  
33 containing energy absorbing enhancers mixed at a 1/1 ratio

1 by weight with mineral oil as the marking material with the  
2 inventive process and exhibiting high contrast from all  
3 viewing angles with no detectable damage to the workpiece  
4 surface. The mark was produced using 5 watts of CW energy at  
5 a beam speed of 200mm/second.

6 FIG. 5 is a photograph of a quartz-glass light bulb  
7 having the mark produced using Cerdec 24-2702 glass frit  
8 containing energy absorbing enhancers mixed at a 1/1 ratio  
9 by weight with mineral oil as the marking material with the  
10 inventive process and exhibiting high contrast from all  
11 viewing angles with no detectable damage to the workpiece  
12 surface. The mark was produced using 5 watts of CW energy at  
13 a beam speed of 200mm/second.

14 FIG. 6 is a photograph of a soda-lime glass microscope  
15 slide having the mark produced using Cerdec 24-2702 glass  
16 frit containing energy absorbing enhancers mixed at a 1/1  
17 ratio by weight with mineral oil as the marking material  
18 with the inventive process to form a 2D symbology mark with  
19 alpha-numeric characters and exhibiting high contrast from  
20 all viewing angles with no detectable damage to the  
21 workpiece surface. The mark was produced using 5 watts of CW  
22 energy at a beam speed of 200mm/second.

23 FIG. 7 is a photograph of a piece of borosilicate flat  
24 panel display glass having the mark produced using Cerdec  
25 24-2702 glass frit containing energy absorbing enhancers  
26 mixed at a 1/1 ratio by weight with mineral oil as the  
27 marking material with the inventive process to form a 2D  
28 symbology mark with alpha-numeric characters and exhibiting  
29 high contrast from all viewing angles with no detectable  
30 damage to the workpiece surface. The mark was produced using  
31 5 watts of CW energy at a beam speed of 200mm/second.

32 FIG. 8 is a chart showing the laser marker parameters  
33 used to produce marks on a variety of substrate materials.

1 FIG. 9 is a drawing of the inventive process in action.  
2 FIGS. 10a through 10d show a 2D profile of a small  
3 portion of the mark produced with the inventive process as  
4 shown in FIG. 6 with an average thickness of approximately 3  
5 microns and a maximum thickness of approximately 14 microns.  
6 Similar results are obtained when using the inventive  
7 process on other substrate materials.

8 Hypothetical Example A

9 The marking materials and substrate described and  
10 illustrated in FIG. 1 above are employed, applying the  
11 marking materials electrostatically as dry particles.  
12 Application of the same laser beam produces markings which  
13 have more even edges, a smoother surface and more uniform  
14 thickness.

15 Hypothetical Example B

16 The marking materials and substrate described and  
17 illustrated in FIG. 1 above are employed, applying the  
18 marking materials electrostatically as liquid droplets.  
19 Application of the same laser beam produces markings which  
20 have more even edges, a smoother surface and more uniform  
21 thickness.

22 Hypothetical Example C

23 The marking materials and substrate described and  
24 illustrated in FIG. 5 above are employed, applying the  
25 marking materials electrostatically as dry particles.  
26 Application of the same laser beam produces markings which  
27 have more even edges, a smoother surface and more uniform  
28 thickness.

29 Hypothetical Example D

30 The marking materials and substrate described and  
31 illustrated in FIG. 5 above are employed, applying the  
32 marking materials electrostatically as liquid droplets.  
33 Application of the same laser beam produces markings which

1 have more even edges, a smoother surface and more uniform  
2 thickness.

3 Before explaining the disclosed embodiment of the  
4 present invention in detail, it is to be understood that the  
5 invention is not limited in its application to the details  
6 of the particular arrangement shown, since the invention is  
7 capable of other embodiments. Also, the terminology used  
8 herein is for the purpose of description and not of  
9 limitation.

10

#### 11 **DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

12 Below follow some basic definitions as used herein:

13 Ceramic and porcelain enamel: A soft melting glass  
14 similar in all cases and like other ceramic glazes, composed  
15 of fluxes and alumino-silicates. Porcelain enamels are  
16 typically used on metallic surfaces.

17 Glass frits: Pre-fused glass material which is  
18 produced by fritting (the rapid chilling of the molten  
19 glassy material), then ground to a powder. Frits are  
20 typically employed as a constituent in a glaze.

21 Mixed metal oxides: An oxide compound containing more  
22 than one metal oxide.

23 Glass frits generally are composed of alkali metal  
24 oxides, alkaline earth metal oxides, silica, boric oxide and  
25 transition metal oxides. In specific, additional  
26 information is known about the commercial marking materials  
27 Cerdec 29-1060 Amber stain, which contains silver sulfide,  
28 copper, copper oxide, barium sulfate, iron sulfide, calcium  
29 hydroxide and crystalline silica. Also, Cerdec 29-1777  
30 Amber stain is also known to contain silver sulfide, copper  
31 oxide, copper-iron sulfide and kaolin clay. Also, Cerdec  
32 29-346 Amber stain is known to contain copper, copper oxide,  
33 silver sulfide, barium sulfate, iron sulfate, iron oxide,

1 and crystalline silica. Also, Cerdec 24-2702 black stain is  
2 known to contain lead borosilicate frit, C.I. pigment black  
3 27 (containing cobalt compounds, iron oxide chromium  
4 compound), C.I. pigment black 30 (containing nickel,  
5 manganese and chromium compounds and iron oxide) C.I.  
6 pigment blue 72 (containing cobalt compound).

7 Comparable mixed metal oxide and glass frit materials  
8 can be secured through manufacturers such as Bayer Company,  
9 Cookson Matthey Zircon, Ferro Corp., Cerdec Corp., E.I.  
10 duPont de Nemours & Co., Hoechst Celanese Corp., and Dow  
11 Chemical Co.

12 The method of this invention is especially suitable for  
13 marking metals, plastics, glasses, and glass ceramics.  
14 Glasses and glass ceramics are well known to the person  
15 skilled in the art and described, for example, in Ullmanns  
16 Enzyklopädie der technischen Chemie, 4th edition, Vol. 12,  
17 pp. 317-366.

18 By ceramic materials are meant inorganic, non-metallic,  
19 high-melting materials that are usually referred to in the  
20 literature as clay ceramics and special ceramics. Examples  
21 thereof are oxides in crystalline or glassy form, e.g.  
22 alkali metal or alkaline earth metal aluminosilicates or  
23 aluminoborates, as well as non-oxides such as carbides,  
24 nitrides, and silicides. For further examples, attention is  
25 drawn to Ullmanns Enzyklopädie der techn. Chemie, 4th  
26 Edition, Vol. 13, pp. 712-716.

27 Glazes are classified chemically as follows:

- 28 1. Bases, the conspicuously fluxing agents,  
29 represented by alkali metal oxides, the alkaline  
30 earth oxides, zinc oxide, lead oxide and many  
31 coloring oxides or chromophoers.
- 32 2. Intermediates, which includes amphoteric oxides, a  
33 group from which alumina is the common example and



1 to which ferric, chromic, manganic, and other  
2 oxides are sometimes assigned. Boric acid is  
3 sometimes considered a member of this group.

4 3. Acids, to which silica, phosphoric oxide, zirconia  
5 and fluorine belong.

6 Glazes are glassy coatings applied to a ceramic  
7 material and having a composition very similar to that of  
8 glass (op. Cit., pp. 722-724). Typical examples of glazes  
9 are those containing quartz, clay, alkali metal oxides,  
10 alkaline earth metal oxides, and low-melting oxides (such as  
11  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{BaO}$ , and  $\text{PbO}$ ) as fluxes.

12 The elements listed on the far left of the Periodic  
13 Table (as now drawn up and widely circulated) are all  
14 elements that form Bases when their oxides are combined with  
15 water, eg,  $\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{NaOH}$  (lye). So do lime ( $\text{CaO}$ ) and  
16 magnesia ( $\text{MgO}$ ). The elements at the right, the non-metals  
17 mostly, form Acids when their oxides combine with water, eg,  
18  $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$  (carbonic acid). The elements in between,  
19 mostly "transition metals", tend to exhibit "amphoteric"  
20 behavior, i.e., they can go either way, depending what else  
21 is close by.

22 A molten glass is chiefly a network made up of silicon  
23 oxide molecules linked together in chains. But at very high  
24 temperature, the silica molecules are free to roam around,  
25 and in a sense behave as a solvent of other molecules.  
26 Alumina ( $\text{Al}_2\text{O}_3$ ) dissolves in this solvent and the combination  
27 is "acidic"; if the molten glaze contains lesser amounts of  
28 basic molecules (the oxides of the alkali metals and the  
29 alkaline earth elements in particular), the glaze will be  
30 classifiable as an acidic glaze, and copper oxide will  
31 impart a green colour to the glaze on cooling (oxidation  
32 conditions only). If, however, there are sufficient  
33 molecules of the basic elements in the mix, the glaze will

1 be said to be basic and in it copper oxide will exhibit a  
2 blue colour (e.g., soda blue of raku).

3 Depending on the utility, the materials to be marked  
4 may be colorless, white, black or colored with a suitable  
5 pigment on which the resulting marking layer additionally  
6 provides contrast or which contains a pigment (e.g. metal,  
7 glass, ceramic or organic colorant).

8 In the practice of this invention, the laser or diode  
9 utilized must provide a relatively low energy level ranging  
10 from 1 to 20 watts at the workpiece surface to be marked.  
11 Commercially available and conventionally powered laser  
12 marking systems operating in either continuous wave or  
13 pulsed mode can be used. For example, a pulsed, Nd:YAG  
14 laser with a maximum capacity of 100 watts and pulse  
15 durations of 5 to 200 microseconds at a frequency of 20 kHz  
16 or higher could be used. However, use of this type of laser  
17 would require reducing the effect of the radiant energy  
18 using mechanical apertures and/or neutral density filters  
19 and/or polarizers and/or de-focusing the beam at the surface  
20 of the workpiece as shown in FIG. 9.

21 The workpiece illustrated in FIG. 6 was created using a  
22 Lumonics Lightwriter™ lamp pumped Nd:YAG laser marker  
23 configured with a 2mm mechanical aperture and a polarizer  
24 which produced a CW beam focused by a 100mm by 100mm flat  
25 field lens to a spot size of approximately 125 microns with  
26 measured power of 5 watts and which was moved by a beam  
27 steering mechanism at a speed of 200mm/second.

28 Additionally, a Uniphase Stablite™ diode pumped Nd:YAG  
29 laser has been used which produced a 700 micron diameter CW  
30 beam focused using a 50mm lens to a spot size of 90 microns  
31 with measured power of 3.1 watts and moved manually at a  
32 speed of approximately 50mm/second.

1 In FIG. 9, the conventionally powered laser beam 100,  
2 105 is de-focused at the surface 109 of the workpiece 106 by  
3 allowing the laser beam 100 to pass through the focal plane  
4 102 and impinge upon the marking material 103 applied to the  
5 surface 109 of the workpiece 106. It has been shown that  
6 placing the workpiece as shown below the focal plane using  
7 the diverging radiant energy 105 is preferred over the use  
8 of the converging radiant energy 100 above the focal plane  
9 102. The resulting spot 104 has a diameter  $d_1$  in the  
10 preferred mode of 5 to 200 microns. The direction of  
11 movement 108 of the diverging laser beam 105 on the surface  
12 of the marking material 103 is shown. A beam steering  
13 mechanism 110 moves the beam. The resulting bonded layer  
14 comprising the mark 107 is shown in contrast to the  
15 remaining non-irradiated marking material 103 on the surface  
16 109 of the workpiece 106.

17 In a preferred embodiment of this invention, a less  
18 expensive, less powerful air-cooled laser which consumes  
19 considerably less electric energy, such as a direct diode or  
20 diode pumped laser is used. Optimal results are generally  
21 obtained using 5 watts of average power with a spot size of  
22 125 microns moving at a speed of 200mm/sec across the  
23 surface of the marking material.

24 Lasers whose parameters can be readily adjusted, for  
25 example, pulse content and pulse duration, permit the best  
26 possible adaptation to the requirements of the marking  
27 material 103 and the composition of workpiece 106 to be  
28 marked. In no case is a preheating of the workpiece 106  
29 necessary. The proper radiant energy is that at which the  
30 marking material absorbs energy most efficiently. It is a  
31 major advantage of the present invention that only a single  
32 pass of the irradiating beam is required to practice the  
33 invention. In all experiments the inventive process was

1 practiced at a room temperature of approximately 70° F.  
2 Furthermore, it is believed that both hot and cold substrate  
3 materials can be marked during their production using the  
4 inventive process.

5 In an alternate embodiment of the invention, the  
6 workpiece may be moved under a stationary laser beam at  
7 similar relative speeds to produce the desired mark.

8 Preferably, the relative speeds taught herein are  
9 executed by the use of a computer controlled workpiece  
10 movement mechanism (not shown) for example, an X-Y and/or  
11 rotary stage using stepper and/or servo motors as supplied  
12 by Newport Corporation and/or a beam steering mechanism (not  
13 shown) for example the HPM™ Scan Head using galvo-mirrors  
14 as supplied by General Scanning, Inc. Alternately, beam  
15 steering can be effected, for example, acousto-optically,  
16 holographically, or by polygon scanners.

17 Some suitable combinations of marking materials and  
18 workpiece composition are listed below:

19  
20 **TABLE I**

21	<b><u>Marking Materials</u></b>	<b><u>Substrate Materials</u></b>
22	1. Glass frit with energy 23 absorbing enhancers and 24 certain colorants and/or 25 pigments including por- 26 celain enamels	Glass, ceramic, porcelain and certain metals including aluminum, brass steel and stainless steel
27		
28	2. Mixed metal oxides with 29 energy absorbing enhancers 30 and certain colorants and/ 31 or pigments	Metals including aluminum brass copper, nickel, tin steel, stainless steel, and certain glasses, ceramics and plastics
32		

1

2 3. Mixed organic pigments Commercial plastics  
3 with energy absorbing including ABS, PVC,  
4 enhancers Nylon™, Delrin™  
5 Teflon™ and Plexiglas™  
6

7 Use of and/or the combination of different compositions  
8 of marking material, second and/or subsequent applications  
9 of marking material and/or the adjustment of laser  
10 parameters will result in variations in the durability,  
11 appearance, and structural form of the resulting mark.  
12 Thus, a person skilled in the art of laser marking can  
13 create a wide variety of marking characteristics to suit his  
14 requirements. All of these marking characteristics can be  
15 achieved with the use of a single low-power, low-cost air-  
16 cooled diode laser. Furthermore, an infinite variety of  
17 colors can be achieved. These features are a significant  
18 advance in the art of surface marking.

19 Preparation of the marking materials, in liquid form,  
20 can, for example, occur through low shear mechanical mixing,  
21 high shear mechanical mixing, ultrasonic mixing and/or  
22 milling. The marking material, in liquid form, can be  
23 manually or automatically applied to the substrate surface  
24 at the desired thickness by hand-spraying it onto  
25 the substrate surface using automated electrostatic spray  
26 equipment. Excess material not bonded to the substrate  
27 surface can be removed by conventional cleaning processes.  
28 In high-volume applications, the unused marking material can  
29 be recovered from the cleaning process and reused.

30 Electrostatic application of marking materials in  
31 liquid and/or aerosol form can be carried out using suitable  
32 electrostatic methods known in the art, according to the  
33 types of substrates to be marked, as discussed above.

1 Different techniques will be appropriate for applying  
2 marking materials to conductive, dielectric or semiconductor  
3 materials.

4 The present invention relates to a method for coating  
5 objects by electrostatic powder-coating, according to which  
6 the dry powder particles or liquid droplets are mixed with a  
7 transporting gas and converted into a fan-shaped spray  
8 before reaching the object to be coated. In the technique  
9 of electrostatic coating, as was emphasized in the U.S. Pat.  
10 No. 3,263,127 (which is incorporated herein by reference), a  
11 fan-spray is of particular interest since the dry powder  
12 particles or liquid droplets, thanks to the fan shape, may  
13 be more easily charged by ion bombardment. Since the duct  
14 carrying the "transporting gas" mixture to the gun is  
15 cylindrical and of small diameter (in general, 7 to 10  
16 millimeters), it is not easy to change such a cylindrical  
17 stream into a homogeneous fan-spray several centimeters  
18 wide. Shaping the stream by simply transforming the shape  
19 of the duct, as shown in U.S. Pat. No. 3,263,127, is not  
20 entirely satisfactory, as the spray obtained is bound to  
21 lack homogeneity on account of the high degree of mechanical  
22 inertia of the dry powder particles or liquid droplets, the  
23 majority of which tend to come out through the center of the  
24 outlet slit, while very few emerge at its edges. Moreover,  
25 if such a nozzle is placed with the fan-spray in a vertical  
26 position, experience shows that due to the effect of gravity  
27 most of the powder particles come out toward the bottom of  
28 the slit.

29 To overcome these drawbacks, there has already been  
30 suggested, as described in U.S. Pat. No. 3,870,232 (which is  
31 incorporated herein by reference), a nozzle equipped with  
32 separate outlet tubes, the dry powder particles or liquid  
33 droplets being sucked into each of them by means of

1 auxiliary air being injected through holes of a given  
2 diameter, which produces perfect homogeneity of the total  
3 spray, whatever the angle of the nozzle. Such a nozzle  
4 functions with a strong air flow, which is advantageous in  
5 certain cases, for example when it is wished to coat at a  
6 distance, but which is often not desired, since a powerful  
7 air flow may prevent the marking material from being  
8 deposited on certain shapes of objects, due to a blowing  
9 effect. Finally, it is well known that greater electrostatic  
10 efficiency is obtained when the dry powder particles or  
11 liquid droplets are slowed down as they leave the nozzle,  
12 thus enabling them to follow the lines of force of the  
13 electric field more easily; a strong axial air flow,  
14 however, increases the axial speed of the stream.

15 The process, as described in U.S. Pat. No. 4,110,486  
16 (which is incorporated herein by reference), makes it  
17 possible to overcome the drawbacks of the previous systems,  
18 and so to produce an electrostatic spraying nozzle which  
19 provides at its outlet a fan-spray of dry powder particles  
20 or liquid droplets, the contents of said spray being  
21 homogeneous whatever its angle may be, and its speed being  
22 slow compared with the speed of the incident "transporting  
23 gas" mixture. It will be appreciated that the marking  
24 material is uniformly suspended in the "transporting gas"  
25 when it leaves the extraction device. If the speed of the  
26 stream of "transporting gas" is high, that is to say greater  
27 than about 15 meters/second, and there are no substantial  
28 bends in the passage leading from the extraction device to  
29 the nozzle, the marking material will remain homogeneously  
30 distributed throughout the "transporting gas" stream  
31 resulting in a uniform application of the marking material  
32 onto the substrate surface.

1  
2                   **Electrostatic Marking Materials**

3           Dry nonconductive powder passes from a hopper by means  
4 of a vibrating plate through an adjustable, nonclogging  
5 extraction device and is directed by means of a stream of  
6 "transporting gas" issuing through a rectangular orifice  
7 from a variable volume plenum chamber into a venturi. The  
8 marking material passes into the venturi and from the  
9 venturi through a discharge nozzle and from the discharge  
10 nozzle onto the substrate to be coated. Corona wires are  
11 located in the proximity of the issuing end of the discharge  
12 nozzle so as to charge the dry powder particles or liquid  
13 droplets in order to direct them onto the substrate.

14           A composition for electrostatic deposition of dry  
15 porcelain enamel frit wherein the frit is reacted with a  
16 flow improving additive containing of an alkoxysilane, and  
17 preferably combined with an adhesion promoting composition  
18 consisting of a silazane is disclosed in U.S. Pat. No.  
19 3,930,062. Additional benefits are also derived if the  
20 sprayed composition also includes a chlorosilane.

21           In support of this disclosure, the following U.S.  
22 Patents are incorporated herein by reference in their  
23 entirety:

24           U.S. 5,698,269 (Electrostatic Deposition of Charged  
25 Coating Particles onto a Dielectric Substrate)

26           U.S. 5,830,274 (Electrostatic Deposition of Charged  
27 Coating Particles onto a dielectric Substrate)

28           U.S. 4,099,486 (Electrostatically Coating Hollow Glass  
29 Articles)

30           U.S. 3,930,062 (Composition and Method for  
31 Electrostatic Deposition of "Dry Porcelain enamel Frit")



1 U.S. 3,558,052 (Method and Apparatus for Spraying  
2 Electrostatic Dry Powder)

3 U.S. 4,110,486 (Electrostatic Powder Coating Method)

4 U.S. 6,063,194 (Dry Powder Deposition Apparatus)

5 6,202,945 (Method and apparatus for electrostatic  
6 powder coating)

7 5,925,419 (Electrostatic powder coating method for road  
8 wheels)

9 5,915,621 (Electrostatic powder coating method and  
10 apparatus)

11 5,811,158 (Method and apparatus for electrostatic  
12 powder coating)

13 5,776,554 (Electrostatic powder coating system and  
14 method)

15 5,747,150 (Electrostatic powder coating method)

16 5,711,489 (Electrostatic powder coating method and  
17 apparatus)

18 5,695,826 (Electrostatic powder coating apparatus and  
19 method)

20 A laminar air flow across the surface of the workpiece  
21 is created by venting and/or exhausting equipment insuring a  
22 consistent localized environment in which the inventive  
23 process can occur.  
24

## Marking Materials

Generally, the marking materials useful in the invention comprise a wide variety of components which can be used alone or in combination to absorb radiant energy, create heat and form (through fusing, sintering or the like) a permanent marking upon a substrate. As discussed elsewhere in this application, the nature of the substrate, the radiant energy source and the components to be used in the marking material must be selected with regard to how they will function together. The finished markings may be visible and/or colored, but may also be invisible under normal light, but visible in other parts of the spectrum such as the IR or UV ranges, and can also be fluorescent and/or luminous.

The marking materials may be specifically described as those materials which, upon application of sufficient laser or diode based energy to produce the necessary heat, bond to glass or ceramic or other substrates to provide an enhanced contrast and/or color marking on the substrate. Low temperature glass frits and the like can be used alone or in combination with other materials.

A wide variety of metal compounds can be used as components of the marking material, generally selected from the oxides, mixed oxides, sulfides, sulfates, carbonates, carbides, nitrides, silicides, and hydroxides of the alkali metals, alkaline earth metals and transition metals. Such compounds can be used to perform at least one function such as absorbing the radiant energy, fusing and/or sintering to form a bond with the substrate.

Representative metals and metal compounds which are expected to be useful include copper, copper oxides, silver sulfide, iron oxides, iron sulfide, iron sulfate, barium

1 sulfate, calcium hydroxide, copper-iron sulfides, silica,  
2 various cobalt compounds and iron-chromium oxides.

3 Examples of suitable inorganic pigments which might be  
4 used are described in Ullmanns Enzyklopädie der techn.  
5 Chemie, 4th Edition, Vol. 14, pp. 1-12, and in the  
6 publication of the Dry Color Manufacturers' Association  
7 (DCMA) "Classification and Description of the Mixed Metal  
8 Oxide Inorganic Colored Pigments", Second Edition, January,  
9 1982. These pigments are "ceramic colorants:", for example,  
10 compounds of oxides of different transition elements or  
11 compounds of oxides of transition elements and of metal  
12 oxides of elements of the main groups of the Periodic  
13 System, e.g., having the spinel-type structure, and also  
14 compounds such as zirconium silicate, zirconium oxide or tin  
15 oxide, the crystal lattice of which contains ions of  
16 transition metals or rare earth metals, as e.g., in  
17 zirconium vanadium blue, in zirconium praseodyme yellow and  
18 in zirconium iron pink, or the cadmium sulfides and cadmium  
19 sulfoselenides as well as inclusion pigments containing such  
20 compounds, e.g., based on zirconium silicate, tin oxide,  
21 zirconium oxide or quartz.

22 Examples of typical ceramic colorants are cobalt  
23 aluminates, chrome tin pink sphere, chrome tin orchid  
24 cassitorite, tin vanadium yellow, zirconium praseodyme  
25 yellow, zirconium iron pink, the cadmium sulfoselenides and  
26 cadmium sulfides and the inclusion compounds containing  
27 them, e.g., zirconium silicate, tin oxide, zirconium oxide  
28 or quartz; copper-red, manganese pink, colcothar, the iron  
29 oxide brown pigments such as iron oxides, iron-chrome-  
30 alumina spinels, manganese-alumina spinels, wine-chrome  
31 spinels, iron-alumina spinels, zinc-iron spinels, nickel-  
32 iron spinels, manganese-chrome spinels, zinc-iron-chrome  
33 spinels, tin oxide, titanium dioxide and titanates, e.g.,

1 nickel-antimony titanate, chrome-antimony titanate or  
2 manganese-antimony titanate.

3 Preferred pigments are zirconium vanadium yellow,  
4 praseodyme yellow, the iron oxide brown pigments such as  
5 zinc-iron-chrome spinels and zirconium iron pink, titanium  
6 dioxide, titanates, cadmium sulfides and cadmium  
7 sulfoselenides as well as inclusion pigments containing such  
8 compounds.

9

#### 10 **Organic Pigments Useful in Marking Materials:**

11 Organic pigments are intensely colored, particulate  
12 organic solids that are essentially insoluble in, and  
13 physically and chemically unaffected by the vehicle or  
14 substrate into which they are incorporated.

#### 15 **Characteristics of Organic Pigments**

16 Bright, pure, rich colors

17 More expensive than inorganic pigments

18 Less resistant to sunlight, humidity, and  
19 chemicals

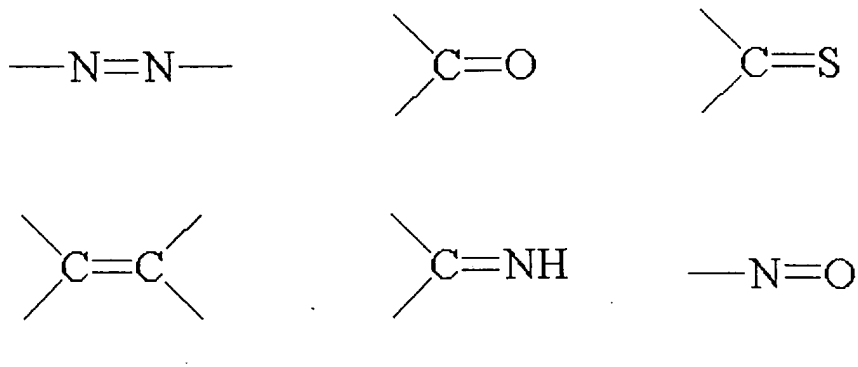
20 Key raw materials are petroleum based

21

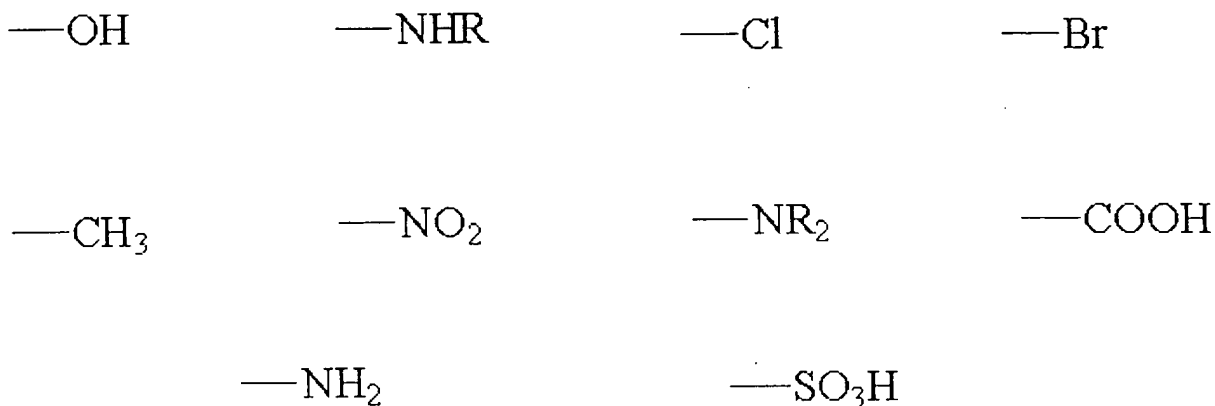
22 Color is produced in compounds by selective absorption  
23 and reflectance of specific wavelengths of the visible  
24 spectrum. Selective effect arise from the presence of  
25 vibrating (resonating) electrons in the structure of a  
26 molecule or molecular group. If a molecule absorbs in the  
27 visible range, it possesses a color complementary to that  
28 which is absorbed. Thus, a compound absorbing in the violet  
29 is seen as yellow. Chemical groups which cause absorption  
30 and give rise to color are called chromophores. Groups  
31 which intensify or modify color are known as auxochromes.

32

1        Some examples of chromophore chemical groups include:



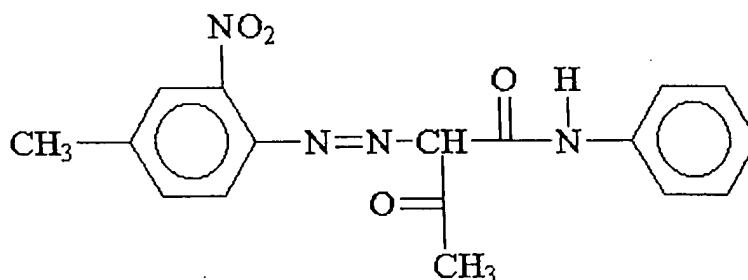
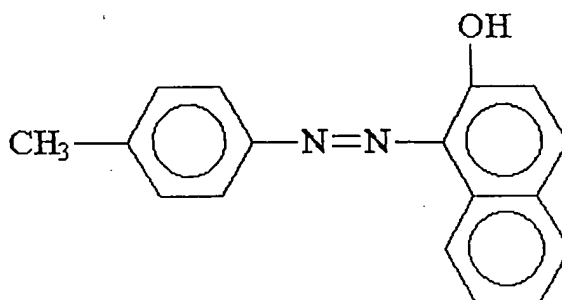
10  
11       Some examples of auxochrome chemical groups include:



25       Organic pigments are divided into six categories:

- 26       1.    Monoazo pigments  
27       2.    Diazo pigments  
28       3.    Acid and base dye pigments  
29       4.    Phthalocyanine pigments  
30       5.    Quinacridone pigments  
31       6.    Other polycyclic pigments  
32  
33

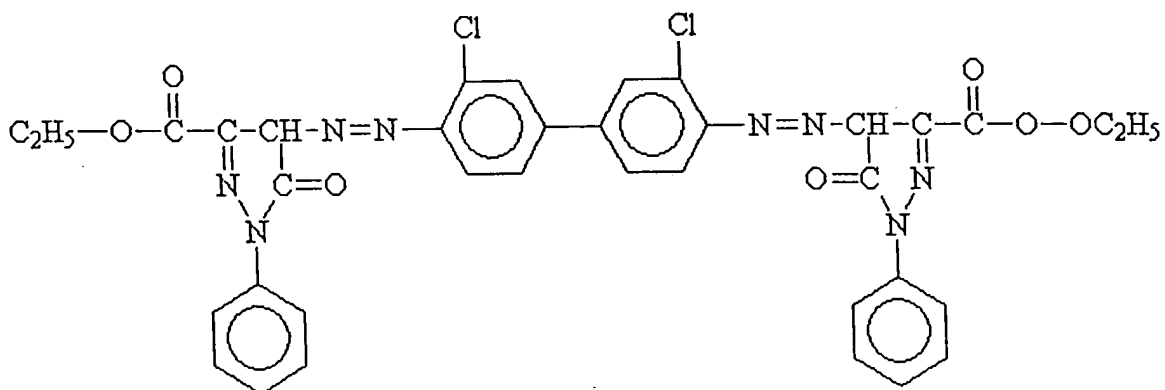
1 Some azo pigments include:



18 Pigment Red 3

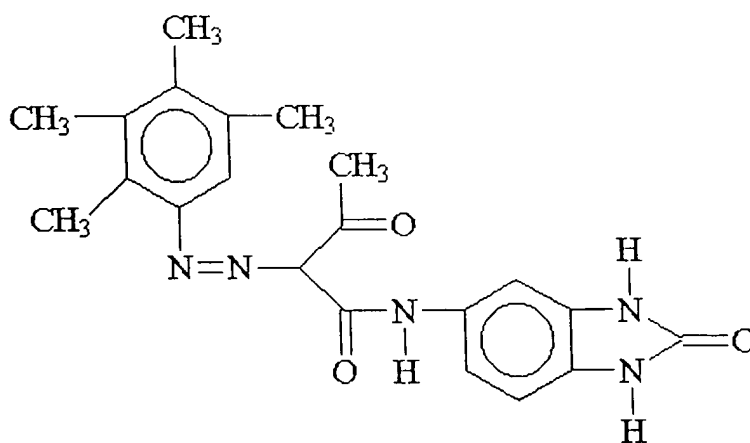
19  
20 Monoazo Yellow

21  
22 Pigment Yellow 12 ( $C_{32}H_{26}Cl_2N_6O_4$ ) is a yellow diazo pigment.  
23 C.I. No. 21090. See diazotization. Preparation:  
24 Condensation of 3,3'-dichlorobenzidine di-diazotate with  
25 acetoacetanilide. Uses: Printing inks; lacquers resistant  
26 to heat and solvents; in rubber and resins; in paper  
27 coloring, textile printing.  
28



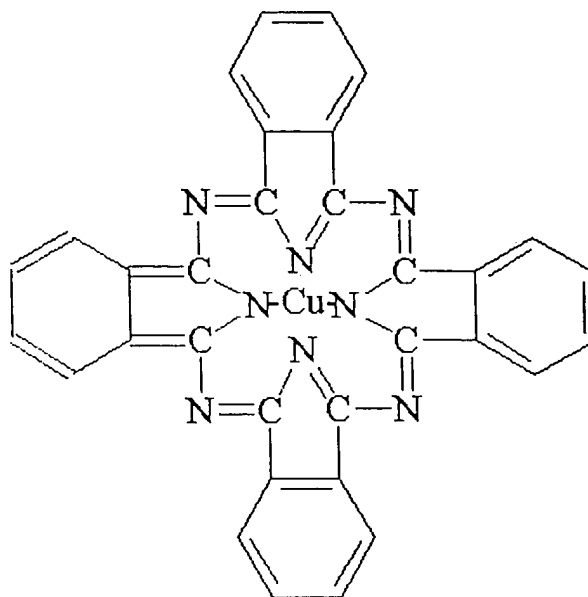
Pyrazolone

#### Benzimidazolone Pigments:



Hansa Yellow

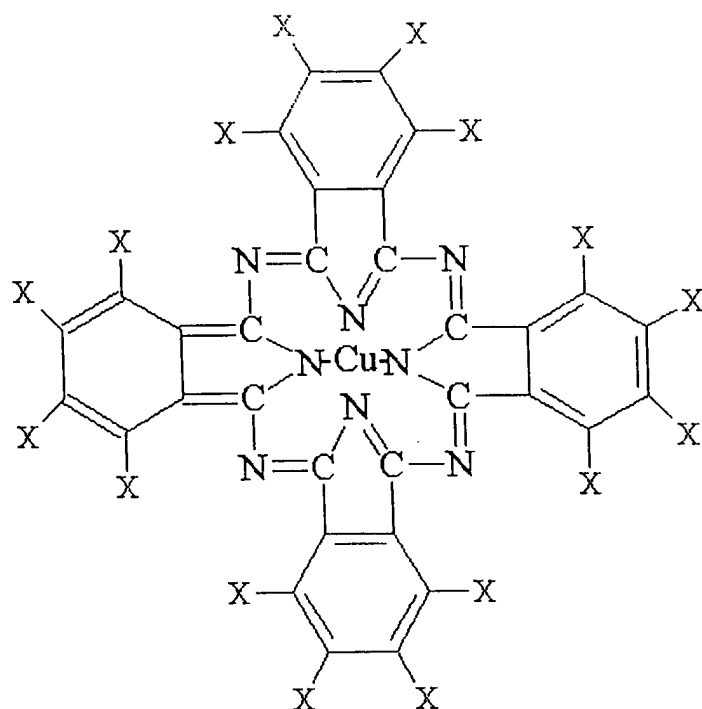
1 Phthalocyanine Pigments are the single most successful class  
2 of organic pigments, and include:



Phthalocyanine Blue

22 Pigment Blue 15 ( $C_{32}H_{16}N_8Cu$ ) is a bright blue copper  
23 phthalocyanine pigment (q.v.). C.I. No. 74160. Preparation:  
24 By heating phthalonitrile with cuprous chloride. Uses: In  
25 paints; alkyd resin enamels; printing inks; lacquers;  
26 rubber; resins; papers; tinplate printing; colored chalks  
27 and pencils.





Phthalocyanine Green

(X = H, Cl or Br, empirical formula  $C_{32}H_xN_8Cl_yBr_zCu$   $x + y + z = 16$ )

Pigment Green 7 ( $C_{32}O_{0-1}N_8Cl_{15-16}Cu$ ) is a bright green chlorinated copper phthalocyanine pigment (q.v.). C.I. No. 74260. Derivation: Heating copper phthalocyanine in sulfur dichloride under pressure. Uses: Paints; printing inks; lacquers; leather and book cloth; paper surfacing; chalks; colored pencils.

Major reasons for use:

- Excellent stability to solvents, heat, light, and weathering
- High tinctorial strength
- Cost effectiveness
- Consistency and uniqueness of shades
- Completely non-toxic

1 Pigment Blue 24 ( $C_{37}H_{34}N_2O_9S_3Na_2$ ) is a bright greenish blue  
2 triarylmethane pigment (q.v.). C.I. No. 42090. Uses: In  
3 printing inks, especially for tinplate printing; in rubber;  
4 plastics; artist colors; lacquers.

5  
6 Pigment Blue 19 ( $C_{32}H_{28}N_3O_4SNa$ ) is a bright blue to bright  
7 reddish navy triphenylmethane pigment (q.v.). C.I. No.  
8 42750A. Use: Coloring for candles.

9  
10 Carbon black, although sometimes classified as  
11 inorganic and not considered to have "positive color value",  
12 is considered an organic pigment for the purposes of the  
13 invention, also functioning as an energy absorbing enhancer.

#### 14 15 **Radiant Energy Sources**

16 Examples of laser or diode based energy sources to be  
17 used are solid state pulsed and/or CW lasers such as ruby  
18 lasers or frequency multiplied Nd:YAG lasers, pulsed lasers  
19 with booster such as pulsed dye lasers or Raman shifter, and  
20 also continuous-wave lasers with pulse modifications (Q-  
21 switch, mode locker), for example, on the basis of CW Nd:YAG  
22 lasers with frequency multiplier or CW ion lasers (Ar, Kr),  
23 as well as pulsed metal vapor lasers; for example, copper  
24 vapor lasers or gold vapor lasers, or high-capacity pulsed  
25 or continuous wave semi-conductor diode lasers, and also  
26 pulsed gas lasers such as CO<sub>2</sub> and excimer lasers.

27 What is generally preferred is a low-power (i.e., about  
28 six watts or less), low-cost continuous-wave diode laser.  
29 Any of the other higher power lasers need to have the power  
30 partially attenuated by known means including mechanical  
31 apertures and/or neutral-density filters and/or polarizers  
32 and/or low-efficiency mirrors.

1       The wavelength to be selected for the laser or diode  
2 based energy source is that at which the marking material,  
3 with or without the energy absorbing enhancer absorbs the  
4 radiation most efficiently.

5       Several different methods are suitable for laser  
6 marking, for example: a) the mask method whereby the area to  
7 be marked is uniformly coated with the marking material and  
8 the radiant energy passes through a fixed, data specific  
9 mask and impinges onto the marking material to produce the  
10 desired mark; and b) the dot-matrix method whereby the area  
11 to be marked is uniformly coated with the marking material  
12 and the radiant energy passes through a computer controlled,  
13 changeable data, dot-matrix mask and impinges onto the  
14 marking material to produce the desired mark; and c) the  
15 beam deflection method whereby the area to be marked is  
16 uniformly coated with the marking material and the radiant  
17 energy passes through a beam steering head and impinges onto  
18 the marking material to produce the desired mark; and d) the  
19 X - Y plotter method whereby the area to be marked is  
20 uniformly coated with the marking material and the radiant  
21 energy moves on a gantry type X - Y mechanism utilizing  
22 mirrors and/or fiber-optics and impinges onto the marking  
23 material to produce the desired mark; and e) the part moving  
24 method whereby the area to be marked is uniformly coated  
25 with the marking material and the workpiece to be marked is  
26 moved using an X - Y motor driven stage under a stationary  
27 beam which impinges onto the marking material to produce the  
28 desired mark; and f) the area irradiation method whereby  
29 data specific marking material is uniformly applied to the  
30 surface of the workpiece and the data specific marking area  
31 is irradiated by means of a beam steering mechanism or by  
32 means of moving the workpiece under a stationary beam. In  
33 methods b), c), d), e) and f) the laser is preferably

1 combined with a laser marking system so that the marking  
2 material can be irradiated with any, e.g., computer  
3 programmed, digits, letters and special symbols where the  
4 laser beam strikes the marking material in the most  
5 efficient manner possible.

6 In one important aspect of the invention, the marking  
7 materials can be formulated to absorb a narrow band of  
8 wavelengths, e.g., approximately 1 micron, and will react  
9 with the substrate material when the proper temperature is  
10 achieved. In this way, a single radiant energy source  
11 (laser or diode) can be employed to mark all materials.

12 Suitable substrate materials which can be marked  
13 include conductive materials, such as:

14 metals, ferrous and non-ferrous, which can be pure  
15 elemental metals, alloys, and include coatings or plating  
16 layers having similar properties; and

17 conductive polymer compositions, which can be  
18 intrinsically conductive due to physico-chemical properties  
19 or filled with conductive fillers, fibers and the like.

20 A variety of nonconductive or dielectric materials are  
21 also suitable for marking, but will normally require coating  
22 with a conductive material before the marking material(s)  
23 are applied by electrostatic methods. For example, all  
24 types of glasses, whether conventional or specialized as  
25 with optical glasses, glasses incorporating nuclear waste  
26 for storage and others, may be employed. Similarly,  
27 ceramics of all types, including those based upon alkali  
28 metal and alkaline earth metal carbonates and the like or  
29 ceramic compounds combining at least two of the elements  
30 carbon, silicon and nitrogen without oxygen can be used.  
31 Various baked porcelain compositions can also be employed.  
32 Semiconductors, which are neither clearly conductive nor  
33 completely dielectric, can also be employed, but may require

1   conductive coatings before electrostatic application of  
2   marking materials.

3       A wide variety of commercial polymeric materials or  
4   plastics can be employed as substrates in the present  
5   invention. A plastic is made up principally of a binder  
6   together with plasticizers, fillers, pigments, and other  
7   additives. The binder gives a plastic its main  
8   characteristics and usually its name. Thus, polyvinyl  
9   chloride is both the name of a binder and the name of a  
10  plastic into which it is made. Binders may be natural  
11  materials, e.g., cellulose derivatives, casein, or milk  
12  protein, but are more commonly synthetic resins. In either  
13  case, the binder materials consist of very long chainlike  
14  molecules called polymers. Cellulose derivatives are made  
15  from cellulose, a naturally occurring polymer; casein is  
16  also a naturally occurring polymer. Synthetic resins are  
17  polymerized, or built up, from small simple molecules called  
18  monomers. Plasticizers are added to a binder to increase  
19  flexibility and toughness. Fillers are added to improve  
20  particular properties, e.g., hardness or resistance to  
21  shock. Pigments are used to impart various colors. Virtually  
22  any desired color or shape and many combinations of the  
23  properties of hardness, durability, elasticity, and  
24  resistance to heat, cold, and acid can be obtained in a  
25  plastic.

26       There are two basic types of plastics: thermosetting,  
27  which cannot be resoftened after being subjected to heat and  
28  pressure; and thermoplastic, which can be repeatedly  
29  softened and remolded by heat and pressure. When heat and  
30  pressure are applied to a thermoplastic binder, the  
31  chainlike polymers slide past each other, giving the  
32  material plasticity. However, when heat and pressure are  
33  initially applied to a thermosetting binder, the molecular

1 chains become cross-linked, thus preventing any slippage if  
2 heat and pressure are reapplied.

3 Some typical plastics are: epoxy resins; polyacrylics;  
4 polycarbonates; polyethylenes; polyolefins; polypropylenes;  
5 polystyrenes; polyurethanes; polyvinyl chlorides; vinyl  
6 plastics. Most of these materials will be dielectrics,  
7 unless they are synthesized or filled to create conductive  
8 materials. Such polymers can be thermoplastic or  
9 thermosetting, and can be solid or slightly pliable under  
10 ambient conditions. Exemplary families of polymers include  
11 the polyethylenes, polypropylenes, polybutenes and various  
12 forms of synthetic and natural rubbers, polyvinyl chlorides,  
13 mylars, nylons, polyarylene sulfides, polystyrenes,  
14 polytetrafluoroethylenes (PTFE), polyacrylates of various  
15 types, and copolymers of many of the preceding. Due to the  
16 generally low level of power used to create the markings,  
17 the methods of the invention can be used to mark cast  
18 objects of trinitrotoluene (TNT) and similar military and  
19 commercial explosives, provided that the objects are first  
20 provided with conductive coatings and the marking materials  
21 electrostatically applied. An advantage of the present  
22 invention is that it provides permanent marking upon  
23 "slippery" plastics such as nylon and PTFE.

24 Although the present invention has been described with  
25 reference to preferred embodiments, numerous modifications  
26 and variations can be made and still the result will come  
27 within the scope of the invention. No limitations with  
28 respect to the specific embodiments disclosed herein are  
29 intended or should be inferred.

30  
31